

# Effect of Ag Particle Size on Electrical Conductivity of Isotropically Conductive Adhesives

Lilei Ye, Zonghe Lai, Johan Liu, *Senior Member, IEEE*, and Anders Thölén

**Abstract**—The present work is to introduce nanoparticles in micro-sized metal particles to study particle distribution in polymer matrix. Previous examinations of the silver-filled particles reveal that the micro-sized particle fillers appear as full density silver flakes, while nanoparticle fillers appear as highly porous agglomerates, similar to open-cell foams. Actually little work has been carried out to study the cross-sectional area of a particle-particle-contact in isotropically conductive adhesives (ICA). In this study, transmission electron microscope is chosen as a main measure to analyze the distribution of different-sized particles. The percentage of the nanoparticles varies from 20 wt% and 50 wt% to full percentage within micro-sized particles, and the total metal content in epoxy resin is 70 wt%. So the change of contact area and contact behavior with various volume ratio of nano-sized and micro-sized particles was investigated. At the same time, the electrical resistivity was measured, which is compared with the different level of the filler loading.

**Index Terms**—Conductivity, isotropically conductive adhesives, micro-sized metal particles, nanoparticles, transmission electron microscopy.

## I. INTRODUCTION

CONDUCTIVE adhesives have been commercially available for decades and consist of highly conductive filler powder dispersed in a flexible, insulating polymer matrix [1], [2]. As the filler concentration is varied, the conductivity exhibits a well known insulator-to-conductor transition which is interpreted as a percolation threshold, and the filled polymer is conducting only when an array of connected conducting particles is formed throughout the materials [3]. So, a continuous linkage of conductive particles is often thought as a single conductive filament, however, this is not accurate. In the case of small particles with diameter of less than 100 nm, particularly those that aggregate in a reticulated structure, some conductivity is observed even in systems where the particles are not in contact [4], [5]. This observation, along with the temperature dependence of the conductivity proposes that a dominant conduction mechanism is carrier tunnelling.

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L. Ye and A. Thölén are with the Department of Experimental Physics, Chalmers University of Technology, Göteborg 412 96, Sweden.

Z. Lai and J. Liu are with the IVF, Swedish Institute of Production Engineering Research, Möln达尔 431 53, Sweden.

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The purpose of present work is to mix both micro-sized and nano-sized-Ag particles as a filler in epoxy resin to observe the contact condition of different sized particles directly using transmission electron microscope, and try to discuss the related conduction mechanism.

## II. EXPERIMENTAL

Samples of Ag-filled adhesive composite material were prepared by mixing the compound together. Three types of silver were used in this study.

- 1) Nano-sized sphere particles approximately 50–150 nm in diameter.
- 2) Micro-sized particles with a diameter of 5–8  $\mu\text{m}$ .
- 3) Flake Ag, of 10  $\mu\text{m}$  in length.

In each case, 70 wt% Ag filler is added to the viscous resin and dispersed. Five series of Ag-filled adhesives with varying particle size were carried out. They are Series I, Ag-flake-filled material, which is prepared as a reference; Series II, micro-sized-Ag particles; Series III, nano-sized Ag particles; Series IV, 50 wt% micro-50 wt% nano-sized-Ag particles; and Series V, 20 wt% nano-80 wt% -micro-sized-Ag particles.

The Ag-filled resins were injected into a section of  $\Phi 3$  mm glass and Al tubing respectively, and then were cured at appropriate temperature. The resistance of all the samples was measured using those injected in the glass tube with the four point method in order to avoid contact resistances. The samples in Al tube were cut with a diamond saw and mechanically ground to thickness of about 100  $\mu\text{m}$ , dimpled and then ion thinned for transmission electron microscope (TEM) observation. TEM experiments were performed with a JEOM 2000 FX microscope.

## III. RESULTS

### A. Measurement of Resistivity

The resistivities of various Ag-filled adhesives are shown in Table I. The resistivity of flake-Ag-filled epoxy resin is  $4.23 \times 10^{-3} \Omega\text{cm}$  and the micro-sized-Ag-particle filled resin has the relatively higher resistivity but still in the same magnitude order,  $7.2 \times 10^{-3} \Omega\text{cm}$ . Although the weight percentage of Ag filler is kept at 70 wt% for all the samples, it is found that the more nano-Ag is introduced to micro-sized particles, the higher resistivity can be obtained. The resistivity is  $0.36 \Omega\text{cm}$  for 20 wt% nano-80 wt% micro-Ag-particle and

TABLE I  
RESISTIVITY OF Ag-FILLED ADHESIVES

Ag-flake	Micro-Ag particle	0.5-micro-0.5-nano-Ag particle	0.8-micro-0.2-nano-Ag particle	Nano-Ag particle
Resistivity (Ohm cm)	$4.23 \times 10^{-3}$	$7.21 \times 10^{-3}$	5.88	0.36

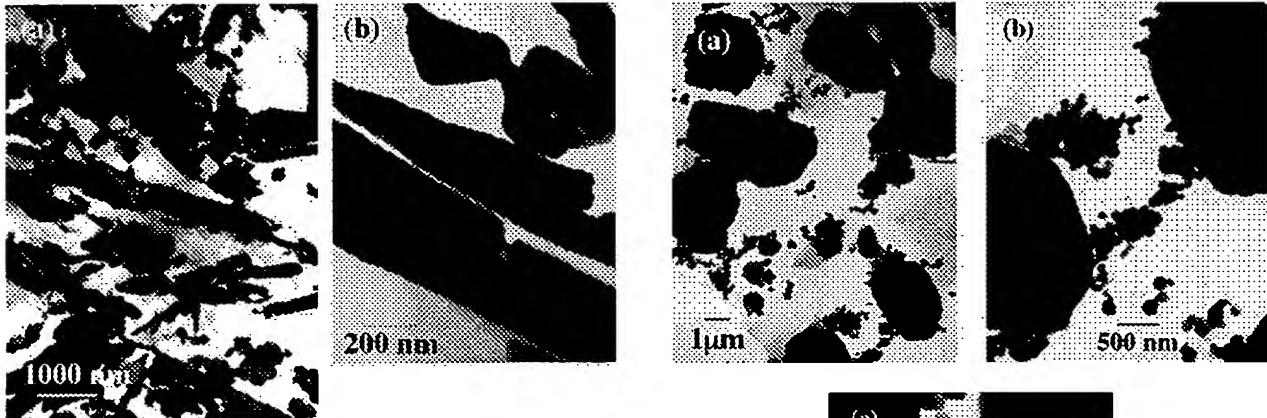


Fig. 1. TEM images of (a) distribution of flake Ag in epoxy resin and (b) The narrow gap between flakes.

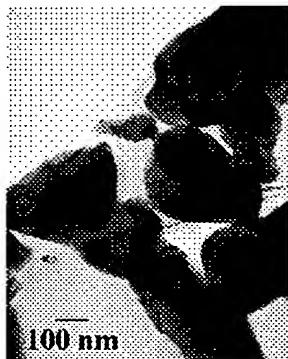


Fig. 2. TEM image of micro-sized Ag particle filled epoxy resin.

5.88 Ωcm for 50 wt% nano-50 wt% micro-Ag-particle in the resin, respectively. When filled with nano-Ag particle alone in resin, the resistance is infinite.

#### B. Microstructure of Ag-Fillers

Fig. 1(a) shows the TEM image of flake Ag in the epoxy resin after curing. It can be seen clearly that flakes come in intimate contact with each other leading to the formation of a continuous linkage. However, it is not true that the flake can contact well everywhere. As shown in Fig. 1(b), between the flakes, there is a narrow gap separating them. The span of the gap is less than 10 nm. The situation of micro-sized particles is similar to that of flakes, which is illustrated in Fig. 2. In the case of 20 wt% nano-80 wt% micro-sized and 50 wt% nano-50 wt% micro-sized particle filled materials, TEM images show different arrangement of particles in Figs. 3-5, separately. With lower content of nano particle in 20 wt% nano-80 wt% micro-sized particle filled sample, the clusters of nano particle "float" among bigger particles. Some of them



Fig. 3. TEM images of (a) 20 wt% nano-80 wt% micro-sized Ag particle filled epoxy resin, (b) the "isolated islands" formed by the cluster of nanoparticles and (c) the connecting "bridge" of nanoparticles.



Fig. 4. TEM image of 50 wt% nano-50 wt% micro-Ag particle filled epoxy resin.

act as bridges to connect big ones [in Fig. 3(b)], and some of them just form isolated islands keeping distance from other particles or clusters [in Fig. 3(c)]. If the sample is tilted several angles on TEM operation, it is found that in some case the contact between nano and micro particles is not real, and there still exists a gap (Fig. 5). So the addition of small particles

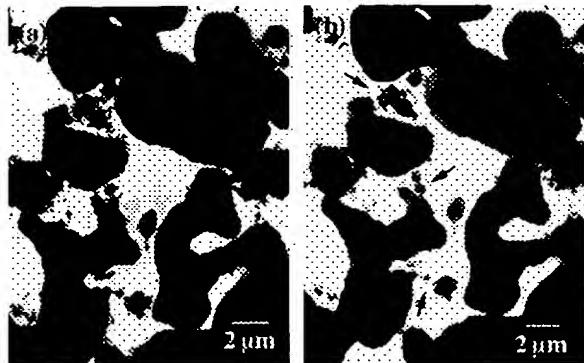


Fig. 5. TEM images of 20 wt% nano-80 wt% micro-sized Ag particle filled epoxy resin, (a) and (b) with different tilting angle. Noting the places marked with arrows.

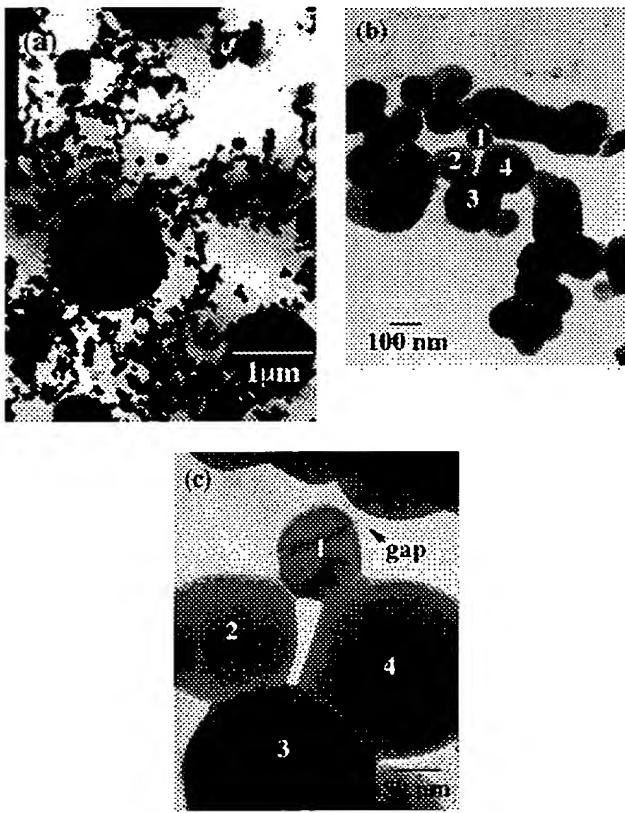


Fig. 6. TEM images of (a) nano-sized Ag particle filled epoxy resin, (b) one cluster in nano-sized Ag particle filled epoxy resin and (c) the same area with the square marked in (a), but with different tilting angle.

provide less possibility to form continuous linkages. Thus there are two phenomena can be observed with comparison of nanoparticle containing and micro-particle-filled composites.

- 1) The chances of direct contact between micro-sized particles is less with the introduction of nanoparticle
- 2) The contact area between nano-and micro-particle is smaller than that between microparticles.

Fig. 6(a) shows the distribution of nano-sized fillers in resin. The continuous conducting path can not be observed in this sample, and the gap existing between clusters can be seen

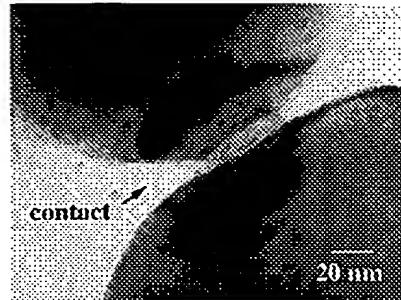


Fig. 7. TEM image of direct contact between nanoparticles.

clearly. From the low magnification of TEM observation [Fig. 6(b)], it seems the nano particles inside one cluster contact well. Actually when the sample was tilted and observed at higher magnification, between particles it still has a space as shown in Fig. 6(c). However, some particles, such as particle 1, 2, 3 and 4, always keep the same position no matter how the sample was tilted. The formation of neck between particles is the result of self-sintering during the powder manufacturing process [6]. In some occasions, the direct contact of small particles can be found as shown in Fig. 7. The formation of fringes around the contact area is the direct proof of intimate contact, which is caused by a plastic interaction between the nanoparticles [7]. Unfortunately, such phenomenon is seldom found in this sample, and it is hard to judge if it originates during the manufacturing or forms in the resin.

#### IV. DISCUSSION

According to the TEM observation, no perfect continuous linkage in all the samples is detected. This means in reality the cross-sectioned area of a particle-particle-contact is much smaller than estimated from simple geometric consideration for isotropically conductive adhesives (ICA). The percolation model predicts that no conduction occurs until one complete conductive path of particles has been created across the sample. Recently several models have been set up to modify the traditional percolation theory, in which the contribution of contact resistance and carrier tunnelling was accounted [8]–[10]. Based on Rusachau Model, the resistance of a contact is the sum of constriction resistance (coming from a direct contact between particle) and tunnelling resistance,

$$R_c = \rho_i/d + \rho_t/a \quad (1)$$

Where  $\rho_i$  is the intrinsic filler resistivity,  $d$  is the diameter of the contact spot,  $\rho_t$  is the tunnelling resistivity and  $a$  is the contact area.

At the present work, when the filler are big particles, such as flake and micro-sized Ag, the chances for direct contact and the diameter of the contact spot are relatively larger, thus the conductivity is dominated by constriction resistance. Wherever, once part of micro-sized particle was replaced by nanoparticle, the diameter of the contact spot between small and big particle becomes extremely small. If the ratio of  $D/d > 10$ , here  $D$  is a given particle size of filler, (1) begins

to diverge so that very high resistances result. Furthermore, it should be noted that if a thin film separating the powders is on the order of 100 Å or less, quantum-mechanical tunnelling can occur, resulting in lower resistivities, otherwise thermionic emission can take place, and causes higher resistivities. The more nanoparticles were added, the more spaces between aggregates, and aggregate and microparticle were formed, then thermionic emission becomes dominant.

## V. CONCLUSION

In this study, transmission electron microscope is chosen as a main experimental method to analyze the distribution of nanoparticle in micro-sized particle sea. It is revealed that the perfect continuous linkage of particles is hard to find and the chance of different contact and contact area becomes less with increasing amount of nano particles. Based on the measurement of resistivity, it is deduced that the conductivity of micro-sized Ag-particle filled adhesives is dominated by constriction resistance, while the nanoparticle-containing adhesives is controlled by tunnelling and even thermionic emission.

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Lilei Ye received the diploma in material science from Institute of Metal Research, Chinese Academy of Sciences, China, and is currently pursuing the Ph.D. degree at Chalmers University of Technology, Göteborg, Sweden.

Her work concentrates on the microstructural observation of lead-free solders and conductive adhesives.



Zonghe Lai received the Ph.D. degree in materials science from the Department of Physics, Chalmers University of Technology, Göteborg, Sweden, in 1994.

He is trained in physical metallurgy and specializes in microstructure studies. He joined IVF, Mölndal, Sweden, after his studies and worked for a number of consortium based research programs in the area of conductive adhesive joining, fine pitch assembly, chip-on-board, and flip-chip technology.



Johan Liu (M'92-SM'96) received the M.S. degree in materials science and engineering and the Ph.D. degree in materials processing technology, both from the Royal Institute of Technology, Stockholm, Sweden, in 1984 and 1989, respectively.

He was associated with IVF Electronics Packaging Research Division, from 1989 to 1999. Since April 1999, he has been a Professor in electronics production at Chalmers University of Technology, Göteborg, Sweden. He serves as the European Editor of the *Journal of Electronics Manufacturing*, IMAPS, the International Advisory Board for Soldering and Surface Mount Technology, and numerous electronics packaging conference committees worldwide. He also chairs the IEEE CPMT Sweden Chapter.



Anders Thößen received the B.S. degree in engineering physics and the Ph.D. in physics from Chalmers University of Technology, Göteborg, Sweden.

He was a Professor in physics at the Technical University of Denmark, Lyngby, from 1973 to 1993, and has been a Professor of materials physics at Chalmers since 1993. His main interests are materials physics and electron microscopy.